The Geometric Factor of Catalysts in the Isotopic Exchange Reaction of Paraxylene with Deuterium Oxide

By Kozo HIROTA and Tomiko UEDA

(Received August 8, 1962)

Since two decades ago, the geometric factor of catalysts have been discussed by Horiuti(1), Beeck(2) and others as an interesting problem in catalysis. However, it is difficult to investigate this factor extensively for lack of such convenient reactions as to fulfill the requirement of investigation.

According to our former reports(3), it has been found promising to use the isotopic exchange reaction of *p*-xylene with deuterium oxide for such purpose, because some catalysts (nickel, nickel-silica, nickel-kieselguhr) can exchange only methyl hydrogen with deuterium while others (platinum, palladium and nickel-alumina) can exchange hydrogen of benzene ring as well as of methyl groups. Such a selectivity now observed can be determined without any knowledge of exchange activities per unit area of each metal. Moreover, the reaction suits the present purpose, by the reason that it is unnecessary to take the electronic factor of metals into consideration. Because even if work function has some connection with the mechanism of both exchange reactions, the selectivity above mentioned would be invariant, as far as their ratio of velocities is concerned.

The research has, therefore, been extended to other metals since the former papers, adopting the same method of research, and a relation was found between the selectivity and the geometric factor of catalysts; i. e., if the ratios of the exchanged degree* of ring hydrogen to that of methyl hydrogen are plotted against lattice constants** of the catalysts, a

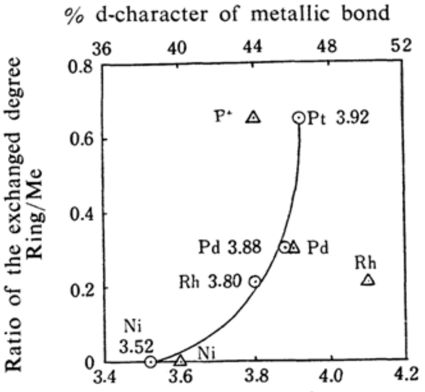

Fig. 1. Relations between exchanged degree and lattice constant or/and d-character of metallic bond (Pauling) for Pt, Pd, Ph and Ni.

⊙ Lattice constans △ d-Character

---

(1) G. Okamoto, J. Horiuti and K. Hirota, *Sci. Pap. Inst. Phys. Chem. Res.*, **29**, 223 (1936).

(2) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

(3) K. Hirota, K. Kuwata and T. Ueda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 362 (1960); K. Hirota and T. Ueda, This Bulletin, 33, 423 (1960); 35, 228 (1962).

* The exchanged degree was determined by the mass-spectrometric and NMR methods.

** R. W. G. Wykoff, "Crystal Structures", Vol. I, Interscience, New York (1948—1958).

monotonous curve is obtained between the two quantities, as shown by the curve in Fig. 1. For the sake of reference the ratios are plotted against Pauling's d-characters of the metals as triangles as shown in Fig. 1. As might be expected, it seems that no relation exists between them.

It will be mentioned here that this relation is perfectly different from the one found by Beeck[2)] in the hydrogenation of ethylene with films of similar metals; i. e., he found a maximum in the curve of logarithms of velocity constant vs. lattice constants of these metals. The present result resembles, however, that of Balandin[4)], who found a linear relation between interatomic distance and activation energy in the dehydrogenation of isopropanol.

Any explanation is not given here to the discrepancy found above, because such an attempt would not be so easy, considering the situation that the reactions to be discussed are not the same in the cases of Beeck, Balandin and the present authors.

We express our thanks to Professor Ryoiti Kiriyama, Osaka University, who kindly taught us the recent data of lattice constants.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

---

4) A. A. Balandin, "Actes de II Congrès International de Catalyse", Technip, Paris (1960), p. 1135.